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**STUDY OF THE BASIC KINETICS
OF DECOMPOSITION OF MMH
AND MHF AND THE EFFECTS
OF IMPURITIES ON THEIR STABILITY**

By DAVID S. ROSS, NORMAN A. KIRSHEN, and DALE G. HENDRY

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FOREWORD

This report presents the results of research performed on AF Contract F04611-69-C-0096 by the Stanford Research Institute, Menlo Park, California 94025, in the period June 16, 1970 to September 15, 1970. The date of submittal is September 15, 1970.

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ABSTRACT

MMH stability in hexadecane solution is sensitive to the presence of transition metal salts. In experiments at 200° in which the ratio of MMH to metal was 90:1, MMH was completely destroyed within five minutes when in the presence of Ni(II), Fe(II), and Fe(III). Cu(II), on the other hand, brought about decomposition at a considerably slower rate--72 percent destruction of MMH in 72 hours. The product distributions in these experiments are dependent to some extent upon the metal salts present. The degree of MMH decomposition in an experiment with Ni(II) was independent of the presence of oxygen. Thus, there appears to be no synergistic effect operating on MMH destruction when MMH is in the presence of both O₂ and a transition metal salt. The surfaces of the metal alloys, aluminums 6061, 1100, 2014; stainless steels 347, 321, and 17-7PH; and inconel X-750, showed no effect on the decomposition of neat MMH in runs at 100°C for 7 days. The acid salts MMH·HNO₃ and MMH·HCl were studied in their respective aqueous acid solutions at 72.8 ± 0.1°C. The hydrochloride salt was perfectly stable over a period of 346 hours. In that period, on the other hand, the hydronitrate salt decomposed to the extent of 73 percent. The products included N₂, CH₃NH₂, NH₃, and C₂H₆. The presence of both N₂ and C₂H₆ suggests the presence of methyl radicals which could result from the formation of CH₃N=NH.

CONDENSED PHASE DECOMPOSITION

Introduction

In this report, we will provide further data on the effects of trace quantities of transition metal ions on MMH stability. During the last quarter we have begun studies on both long-term and short-term effects of metal surfaces on the decomposition of neat MMH. The results discussed deal with the surfaces of several metal alloys. Lastly, the stabilities of both the hydronitrate and hydrochloride salts of MMH have been studied.

Effect of Trace Metal Ions on the Decomposition of MMH Solutions

In the last quarterly report (June 15, 1970), we reported that acetylacetonates or stearates of Fe(III), Fe(II), Cu(II), and Ni(II) completely decomposed MMH in hexadecane solution at 320°C in less than 3 hours. To compare the relative catalytic abilities of these active salts, we have sought an intermediate temperature where the decomposition reactions proceed less rapidly, yet fast enough for accurate comparison.

Results and Discussion. Based on preliminary experiments, the decomposition of 0.090 M MMH in hexadecane was followed at 200° in the presence of 0.001 M Cu(II) acetylacetone over a 72 hour period. The proportion of products was constant over the time studied. The half life under these conditions was about 53 hours. In the absence of Cu(II), earlier experiments showed about 5 percent decomposition during this time interval.

Using the same experimental conditions, the reaction was run in the presence of Ni(II), Fe(II), and Fe(III) for 24 hours, and total

decomposition was found. In subsequent experiments, reaction times as short as 5 minutes also gave complete decomposition. Thus, these Ni and Fe salts are at least 10^3 times as effective as Cu salts in decomposing MMH under these conditions. The data are summarized in Table I. Further comparison of these salts will be made using neat MMH.

Table I

DECOMPOSITION OF 0.000 M MMH IN THE PRESENCE
OF 0.001 M Cu(II), Ni(II), OR Fe(III)
AT 200°C IN HEXADECANE

Run	Time (Hrs)	MMH Decomp (%)	ΔMMH (μmoles)	Products - μmoles				
				N ₂	CH ₄	H ₂	CH ₃ NH ₂	NH ₃
Cu(II)-3	24	25.0	45	23.0	19.8	0.1	33.1	39.0
Cu(II)-4	48	48.0	83	32.8	29.8	0.2	41.5	54.0
Cu(II)-5	72	72.0	106	41.8	35.8	0.3	51.0	70.5
XVII-Ni(II)-6	0.08	100	180	74.9	59.0	0.1	100	86
XVII-Ni(II)-5	0.25	100	180	81.1	58.4	1.2	109	90
XVII-Ni(II)-1	24	100	180	89.3	74.2	0.4	125	87
XVII-Fe(III)-5	0.25	100	180	---	---	---	---	---
XVII-Fe(III)-1	24	100	180	98.4	100.8	0.1	109	87

The product distribution appears to be somewhat characteristic for each metal. The significance of the patterns is not clear; for example, methylamine predominates when Ni and Fe salts are present, and ammonia predominates when Cu is present.

Decomposition of MMH in Presence of Ni(II) and O₂*

We have performed some experiments to determine if there were any synergistic effects on MMH stability of transition metal ions and oxygen. Accordingly, we have run reactions of oxygen and MMH in the absence and presence of 2 μ mole of Ni(II) stearate.

Results. Reaction tubes were loaded with 2 ml 0.01 M Ni(II) stearate in hexadecane and 180 μ moles MMH. Then, while each tube was held at -78°C, 43 μ moles of O₂ was added by bringing the pressure in the tube up to 100 mm as measured on the Wallace and Tiernan absolute pressure gauge. The tubes were sealed off. Two control tubes were prepared identically, with the exception that no Ni(II) stearate was used. The four tubes were allowed to stand at room temperature for 24 hours and then analyzed.

The results of these experiments (Table II) show that the amount of decomposition of MMH is not significantly enhanced by the presence of Ni(II) stearate.

Table II

REACTION OF MMH (180 μ moles) AND OXYGEN (43 μ moles)
IN THE PRESENCE AND ABSENCE OF NICKEL(II)
STEARATE (2 μ moles) AT ROOM TEMPERATURE FOR 24 HOURS

Nickel(II) Stearate	MMH Decomp (μ moles)	Product Data			
		N ₂	CH ₄	O ₂	CH ₃ OH
No	52.5	55.3	43.4	0.04	7.0
No	48.6	46.7	30.1	0.72	6.0
Yes	49.4	40.65	34.0	0.29	5.0
Yes	37.0	--	--	--	6.0

* In our last quarterly report (June 15, 1970), we stated that MMH disappeared to the extent of ~9% in the presence of Ni(II) at room temperature for 24 hours. This result was anomalous, as a repeat run resulted in no decomposition of MMH.

Effects of Metal Surfaces on the Decomposition of Neat MMH

We have completed some of our preliminary study of the effects of metal surfaces on the decomposition of neat MMH. The metals we are examining include pure metals (Al, Fe, Ti, Mo, and Cr) and alloys (stainless steels 321, 347, 17-7PH; aluminums 6061-T6, 1100, 2014-T6; inconel X-750). To date only the reactions of the alloys with MMH which were run at 100° for 7 days have been completed.

Procedure. The studies are performed in reaction tubes with break seals to provide for analysis of gaseous products. The tubes are prepared with the sample end open to allow the insertion of metal specimens. The specimens, which have dimensions 6 x 25 mm with thicknesses varying from 5 to 30 mils, are weighed and inserted into the tubes after cleaning with trichloroethylene, HNO₃, water, 1% EDTA disodium salt in water, and finally water again. The bottom ends of the tubes are sealed and the tubes weighed. The tubes are then transferred to the dry box where approximately 1 ml of Olin Propellant grade MMH is dispensed into each tube. The tubes are degassed, sealed under vacuum, and weighed again. In this manner the exact weight of MMH dispensed into each tube is known.

Four tubes have been prepared for each of the pure metals. Two of them are now being run at 50°, one at ambient temperature, and one has been run for a week at 100°. One tube for each metal alloy has been prepared and run for one week at 100°. The results of the latter 100° runs are reported below.

Results. Table III contains the analyses for the runs at 100° with the various alloys. The results are quite similar to the control run without any metal which in turn is very similar to the control run at 150°. The presence of azomethane has been determined by both glpc and mass spec analyses. While the nature of the chemistry that is occurring is not clear, only very small amounts of decomposition are observed, and that is largely not related to the metal surfaces. Thus MMH is compatible with these alloys up to at least 100° for a period of one week.

Table III

EFFECT OF ALLOYS ON STABILITY OF NEAT MMH RUN
FOR 7 DAYS AT 100°C^a

Metal Surface	Products, ^b μ moles/g sample				Percent Dec. ^c
	$\text{CH}_3\text{N} = \text{NCH}_3$	NH_3	CH_3NH_2	Non Cond. -195°	
None	32.1	22.2	7.8	>1.0	0.32
z (150°)	31.6	36.2	29.0	>1.0	0.36
Al 6061	31.9	32.3	10.8	0.5	0.33
Al 1100	32.7	32.3	13.4	0.5	0.35
Al 2014	33.6	33.9	12.0	0.3	0.36
SS 347	31.2	37.8	10.8	0.5	0.33
SS 321	--	--	10.8	0.5	--
SS 17-7	31.5	31.5	14.1	0.5	0.35
Inc. X-750	32.1	34.6	10.0	0.5	0.34

^a Reactions were carried out with 330 mm^2 of metal surface plus approximately 1.0 ml of Olin Propellant Grade MMH.

^b The MMH initially contained the following amounts of $\text{CH}_3\text{N}=\text{NCH}_3$, NH_3 , and CH_3NH_2 : 0, 24, 2.7 μ mole/g sample.

^c Decomposed MMH estimated from methyl groups in products; correction is made for initial CH_3NH_2 .

Acid Salts of MMH

Both MMH·HCl and MMH·HNO₃ have been studied in aqueous solutions of the respective mineral acids. The effects of both strong acid and differences in basic anion could thus be determined.

Experimental. The studies were carried out in sealed and evacuated nmr tubes, each containing degassed solutions of the salt, as well as capillary tubes filled with tetramethylsilane (TMS). Each tube was affixed to a vacuum line after receiving 0.5 ml of either 4.17 M HCl or 4.18 M HNO₃. The acids were degassed, and 50 mg of MMH (degassed) was

then transferred to the liquid nitrogen cooled tubes under vacuum. The MMH:acid ratio was then roughly 1:2. The tubes were then sealed off and allowed to warm slowly from the top down. Thus the MMH in each case smoothly dissolved the still partially frozen acid. The tubes were then tilted back and forth several times for mixture, and the zero-time spectrum was run. The tubes were then put into a bath kept at $72.8 \pm 0.1^\circ\text{C}$, pulled at intervals, and the spectra taken.

The spectrometer was "locked" onto water, and the TMS peak was used as a standard for peak integration. The acid solutions of MMH displayed a singlet at ≈ 6.9 . This peak, the methyl hydrogen resonance, was the only one seen for the molecule as the N-H resonances were obliterated because of rapid proton exchange with solvent.

Results. The experiment was run for a total of 346 hours, and in that period the chloride salt showed no detectable signs of decomposition. The nitrate salt, on the other hand, had decomposed to the extent of 73 percent. Table IV provides the details of the reaction progress, and these data roughly fit a plot that is first order in both MMH and acid, although they would likely fit higher order plots also.

Table IV

DECOMPOSITION OF 2.18 M MMH HNO₃ IN 2.00 M HNO₃
AT $72.8 \pm 0.1^\circ\text{C}$

Time (hr)	Decomposition (%)	Time (hr)	Decomposition (%)
20	18	269	67
134	53	346	73
175	55		

The NMR tube was broken open under vacuum, and the volatile products were determined quantitatively:

Initial MMH	=	1090 μ moles
Δ MMH (by nmr)	=	795 μ moles
N_2	=	208 μ moles
C_2H_6	=	14 μ moles
NH_3	=	137 μ moles
CH_3NH_2	=	29 μ moles

In addition, qualitative analysis by vpc of this aqueous solution showed the presence of CH_3OH and CH_3NO_2 . At least 11 other products were noted in the gas chromatograph, and the peak "profile" was similar to that seen from a sample of MMH exposed to air and thus oxidized.

The presence of ethane clearly suggests the presence of methyl radicals, and the relatively large quantity of N_2 indicates that initial oxidation to $CH_3N=NH$ is a reasonable proposition. The large number of oxidation products indicates that the detailed oxidation process is rather complex.

The results clearly point to the fact that $MMH \cdot HNO_3$ in aqueous solution is unstable. Since both the chloride and nitrate solutions were at about the same acidity,* the differences in stability must be due solely to the effects of the different anions. Clearly the oxidizing ability of nitrate is an important factor in the relative instability of $MMH \cdot HNO_3$ and it would appear that consideration be given this point vis-a-vis storage of MMH and nitrate salts.

* The Hammett acidity function (H°) values for the hydrochloric and nitric acid solutions are -1.47° and -1.38 , respectively. See M. A. Paul and F. A. Long, Chem. Rev. 57, 1 (1957).

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